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Direct preparation and structure determination of tertiary and secondary amine boranes from primary or secondary amine boranes

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Abstract

New secondary and tertiary amine borane derivatives were prepared in a one-pot reaction starting from primary amine boranes. The reaction involves treatment of an amine borane with 2 equivalents of *s*-BuLi at −78 °C. In general, mixtures of mono and di metallated products were obtained. Alkyl iodides and benzyl chloride reacted with the lithiated amine, but aldehydes and ketones were reduced. Conversion was high as determined by NMR, but moderate to low yields were obtained after chromatography, possibly due to decomposition on silica. Crystal structures were obtained for the compounds **3a**, **3b** and **3c**.

Keywords: *Sec*-amine borane; *tert*-amine borane; N-deprotonation; X-ray structures

1. Introduction

Deprotonation of tertiary [1] and secondary [2] amine boranes is a well known method used to prepare valuable intermediates in organic synthesis [3]. Various applications of such compounds were published in the literature such as their use in aqueous reduction of aldehydes and ketones [4], reductive amination [5], olefin hydroboration [6] and amide reduction [7]. They are also widely used in palladium catalyzed systems [8–10], as well as chiral transfer reagents [11], as activators for α-deprotonation of tertiary amines [2e,12], and as protective groups against nitrogen lone pair oxidation [13]. Boron complexation facilitates N-deprotonation due to the covalent attachment to the nitrogen atom of the amine [14–16]. Because of the contrasting regiochemistry in metallation of these compounds, the use of amine borane complexes introduced a new route in preparation of new amine borane derivatives which in turn were converted to the free amines in ethanolic acidic conditions. In a recent review on the previously published work in this field [20], no methods were reported for the preparation of tertiary amine boranes directly from primary amine boranes by reaction with simple alkyl or benzyl halides. In this work, we report a new direct method for the synthesis of secondary and tertiary amine boranes starting from primary amine boranes, using N-deprotonation. In some cases crystals were obtained for some compounds and their structures were determined by X-ray diffraction.

2. Results and discussion

2.1. Syntheses

Treatment of a primary or secondary amine borane **1** with 2 equivalents of *s*-BuLi in THF at −78 °C then

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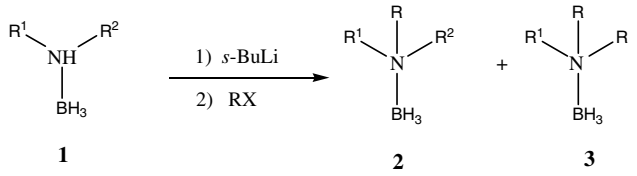

Scheme 1. Substitution of amine borane complexes **1** via metallation.

warmed to room temperature, followed by cooling to −78 °C and addition of an alkyl iodide or benzyl halide gave two products, the mono alkylated **2** and the double alkylated **3** adducts (Scheme 1). The need to use excess of *s*-BuLi was necessary because using fewer than two equivalents resulted in a complex reaction, with recovery of unreacted starting material. We suspect that it may be due to the known instability of organolithium reagents in THF [17]. It is also possible that some limited destruction of the borane complexes occurred by nucleophilic attack of *s*-BuLi resulting in partial consumption of the base. It is also suspected that this may be partially due to the high affinity of these complexes for water. *n*-BuLi was ineffective [12,16], and led to a very complex reaction mixture and low yields. Using ether as solvent gave similar results.

With MeI, only the dialkylated product was obtained (Table 1, entries **a**, **e**, **h**). For more hindered electrophiles (*n*-PrI) both **2** and **3** were obtained, while **3** is the major product (entry **b**). However, with *n*-BuI, the mono inserted adduct **2** was the major product (entry **c**). We suspect that the reaction is controlled mainly by steric considerations. When a hindered amine borane (iPr–$NH_2 \cdot BH_3$) was reacted with *n*-PrI and *n*-BuI, the mono alkylated species **2**, became the major product (entries **f**, **g**). When a very bulky amine complex was used (*t*-Bu-$NH_2 \cdot BH_3$), the only product obtained was the mono alkylated species, **2** (entries **i**, **j**). Benzyl chloride gave the mono inserted adduct in low yield with recovery of the starting complexed amine and the electrophile (entry **d**). Secondary amine borane were less reactive. Indeed (iPr_2–$NH \cdot BH_3$) reacted only with MeI (entry **k**). Thus when the amine complex or the electrophile are bulky, the mono adduct **2** is the major product. The products were obtained either as solids or oils. The majority of the products were purified by flash chromatography, which decreased the quantitative yield substantially. Some of these purified products were crystallized from THF. On the other hand, several products could not be eluted from silica (entries **2b**, **2c** and **2d**) so the spectral data for them was reported for the crude mixtures (see Tables 1 and 3).

Table 1
Tertiary and secondary amine boranes, prepared from primary amine boranes **1**

Entry	R^1	R^2	RX	Isolated yields (%)		Yield by NMR (%)
				2	**3**	
a	$PhCH_2$	H	CH_3I	0	45	>99
b	$PhCH_2$	H	*n*-PrI	25	75	>99
c	$PhCH_2$	H	*n*-BuI	–	35	>99
d	$PhCH_2$	H	$PhCH_2Cl$	0	–	35
e	iPr	H	CH_3I	0	25	>95
f	iPr	H	*n*-PrI	31	15	>99
g	iPr	H	*n*-BuI	28	18	>99
h	*t*-Bu	H	CH_3I	0	40	60
i	*t*-Bu	H	*n*-PrI	25	0	60
j	*t*-Bu	H	*n*-BuI	30	0	80
k	iPr	iPr	CH_3I	15	0	80

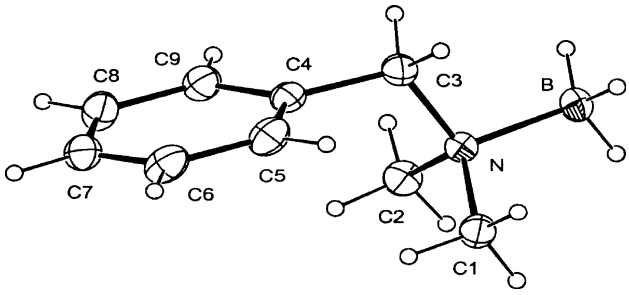

Fig. 1. Molecular structure of **3a** in the crystal.

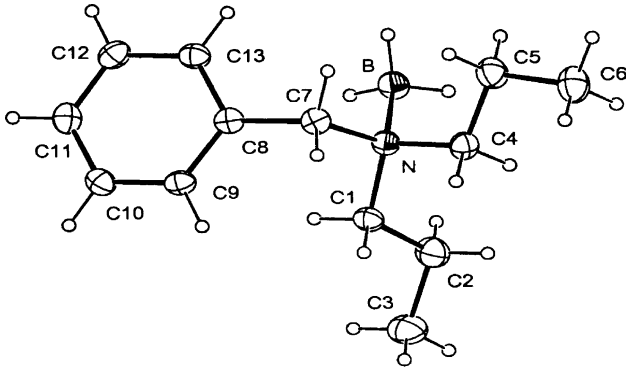

Fig. 2. Molecular structure of **3b** in the crystal.

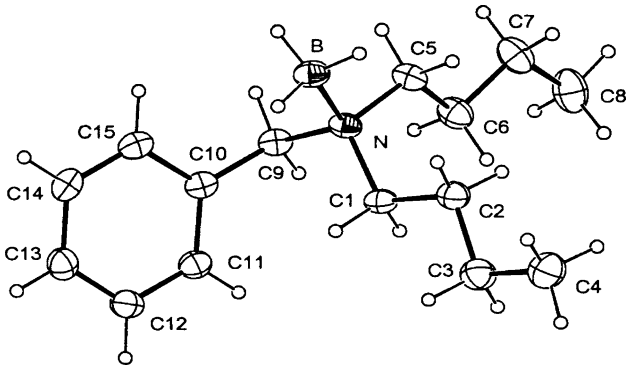

Fig. 3. Molecular structure of **3c** in the crystal.

Table 2
Crystal data and structure refinement for compounds **3a**, **3b** and **3c**

	Compound **3a**	Compound **3b**	Compound **3c**
Empirical formula	$C_9H_{16}BN$	$C_{13}H_{24}BN$	$C_{15}H_{28}BN$
Formula mass (g mol^{-1})	149.04	205.14	233.19
Habit	Prisms	Plates	Needles
Color	Colorless	Colorless	Colorless
Temperature (K)	110(2)	110(2)	110(2)
Radiation	Mo Kα	Mo Kα	Mo Kα
Crystal size (mm)	$0.35 \times 0.30 \times 0.20$	–	–
Crystal system	Orthorombic	Monoclinic	Monoclinic
Space group	*Pna21*	*C2/c*	*P21/c*
a (Å)	20.07900 (10)	24.3900(7)	13.8450 (3)
b (Å)	5.9570 (2)	5.8380(2)	5.99800 (10)
c (Å)	7.8770 (5)	19.0350(7)	18.8290 (6)
α (°)	90.00	90.00	90.00
β (°)	90.00	104.7500(11)	104.1590 (9)
γ (°)	90.00	90.00	90.00
V (Å^3)	942.17 (7)	2621.05(15)	1516.10 (6)
Z	4	8	4
D_{calcd} (g cm^{-3})	1.0507	1.0397	1.0216
F(0 0 0)	328	912	520
μ (mm^{-1})	0.059	0.058	0.057
2θ range (°)	1.41–27.88	1.73–27.83	1.41–28.28
Number of unique reflections	1197	2933	3611
Number of restraints	1	0	0
hkl limits	0–26, 0–7, 0–10	0–31, 0–6, −24 to 24	0–18, 0–7, −14 to 23
Number of parameters	103	139	157
Number of reflections with [$I > 2\sigma(I)$]	1107	2068	2468
Final *R* indices[a] [$I > 2\sigma(I)$]	0.0396	0.0553	0.0574
R_1[a]	0.1050	0.1248	0.1307
wR_2[b]			
$\lvert\Delta\rho\rvert$ (e Å^{-3})	⩽0.216	⩽0.224	⩽0.257
GOF	1.040	1.028	1.020

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.
[b] $wR_2 = \left\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\right\}^{1/2}$.

Table 3
Selected bond length (Å) and angels (°) for compounds **3a**, **3b** and **3c**

	Compound **3a**	Compound **3b**	Compound **3c**
B–N	1.620(2)	1.623(2)	1.627(19)
N–C1	1.490(2)	1.5097 (18)	1.5109 (19)
N–C3	1.514(2)	–	–
N–C7	–	1.5197(19)	–
N–C9	–	–	1.5204(19)
B–N–C	108.70(13)	111.54(11)	111.08(11)
N–B–H	109.5	109.5	109.5
C–N–C	108.66(14)	107.98(11)	112.03(11)
C–N–B	108.70(13)	111.54(11)	111.08(11)

2.2. Crystal structure analyses

Crystals suitable for X-ray structure determination were obtained for compound **3a**, **3b** and **3c**. Their molecular structures were determined by single-crystal X-ray diffraction. The results of the diffraction analysis, crystal data, and details of the structure determination are shown in Figs. 1–3, and the data are summarized in Table 2.

Molecular structures of the three compounds **3a**, **3b** and **3c** were determined at ca. 110 K with relatively high precision. They represent three independent and internally consistent determinations. The covalent parameters exhibit standard values characteristic to boron in tetrahedral sp^3 hybridization. The conformation around the boron atom is nearly ideally tetrahedral, with N–B–H bond angles of 109° (Table 2).

3. Conclusions

A series of secondary and tertiary amine boranes were prepared in good to excellent yields in a short time reaction and high purity, using a one-pot operation, starting with an alkyl amine borane or benzyl amine borane and treated with the appropriate electrophile. The molecular structures of **3a**, **3b** and **3c** were determined by single-crystal X-ray diffraction. Studies are presently directed at examining the scope of this approach with more complicated electrophiles, and determining their biological activity.

4. Experimental

4.1. Syntheses

4.1.1. General comments

All reactions were carried out under a dry nitrogen atmosphere in oven-dried glassware. Solvents were dried over sodium/benzophenone and freshly distilled before use. All other chemicals were obtained from Sigma–Aldrich and used as received without any further purification. All amine boranes complexes were prepared from borane methylsulfide and the corresponding amine using the literature method [18].

Melting points were determined on a Fisher scientific melting point apparatus. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Varian Unity spectrometer (300, 75, 96 MHz), respectively. Chemical shifts were recorded relative to an internal standard Me_4Si for ^{1}H and ^{13}C NMR and $Et_2O \cdot BF_3$ as an external standard for ^{11}B NMR. Data were reported in the following order: chemical shifts are given in δ (ppm); multiplicities are indicated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *dd* (doublet of doublet); coupling constants, *J*, are reported in hertz. Liquid chromatography was performed using column chromatography of the indicated solvent system on Merck silica gel 60 (0.040–0.063 mm).

4.1.2. General procedure

A solution of *s*-BuLi in cyclohexane (1.3 M, 2 mmol) was added drop wise to a solution of benzylamine borane (0.121 g, 1 mmol) in THF (10 ml) at −78 °C. The solution was stirred for 30 min at −78 °C, then it was allowed to warm up to room temperature for 30 min, before recooling down to −78 °C and addition of CH_3I (0.125 ml, 2 mmol) in one portion. After 5 min the cooling bath was removed, and the reaction mixture was stirred for 1 h at room temperature. A saturated $NaHCO_3$ solution (10 ml) was added where the aqueous layer was extracted with ether (3 × 10 ml); the combined organic layers were after dried over sodium sulfate. After evaporation of the solvents the residue was purified by flash chromatography on silica gel (10% EtOAc in petroleum ether) to give (***3a***) *N,N,N-dimethylbenzylamine borane* as white solid m.p. = 101 °C (68 mg) 45% yield, ^{1}H NMR ($CDCl_3$): δ 1.23–2.60 (v.*br* BH_3), 2.50 (*s*, 6H), 3.98 (*s*, 2H), 7.25 (*m*, 5H). ^{13}C NMR ($CDCl_3$) {H}: δ 49.62, 67.51, 128.45, 129.10, 131.20, 131.19. ^{11}B NMR ($CDCl_3$): δ −9.46 (*q*, J_{B-H} = 96.86). *Anal.* Calc. for $C_9H_{16}NB$: C, 72.48; H, 10.73; N, 9.39. Found: C, 72.50; H, 10.75; N, 9.42%.

4.1.3. N,N-propylbenzylamine borane (*2b*)

White solid in mixture with the *N,N,N*-dipropylbenzylamine borane, it could not be isolated so the only data could be recorded from the mixture was. ^{1}H NMR ($CDCl_3$): δ 0.80–2.20 (v.*br*, BH_3), 0.84 (t, 3H), 1.53 (*m*, 2H), 2.42 (*t*, 2H, *J* = 15), 3.60 (*s*, 2H), 7.28 (*m*, 5H).

4.1.4. N,N,N-dipropylbenzylamine borane (*3b*)

White solid, m.p. = 85 °C, 25% (53 mg) yield. ^{1}H NMR ($CDCl_3$): δ 0.88 (*t*, 3H, *J* = 14.7), 1.20–2.10 (v.*br* BH_3), 1.86 (*m*, 2H), 2.57 (*t*, 2H, J_{H-H} = 16.8), 3.96 (*s*, 2H), 7.35 (*m*, 5H). ^{13}C NMR ($CDCl_3$) {H}: δ 11.79, 17.17, 60.87, 63.45, 128.46, 129.04, 131.83, 132.49. ^{11}B NMR ($CDCl_3$): δ −13.56 (*q*, J_{B-H} = 87.84). *Anal*. Calc. for $C_{13}H_{24}NB$: C, 76.09; H, 11.70; N, 6.83. Found: C, 76.11; H, 11.69; N, 6.80%.

4.1.5. N,N-butylbenzylamine borane (*2c*)

White solid in mixture with the *N,N,N*-dibutylbenzylamine borane, could not be isolated so the data were recorded from the mixture. ^{1}H NMR ($CDCl_3$): δ 0.80–1.80 (v.*br*, BH_3), 0.87 (*t*, 3H, J_{H-H} = 14.4), 1.28 (*m*, 2H), 1.44 (*m*, 2H), 2.39 (*t*, 2H, J_{H-H} = 14.7), 3.54 (*s*, 2H) 7.29 (*m*, 5H). ^{13}C NMR ($CDCl_3$) {H}: δ 14.02, 20.55, 29.04, 53.11, 58.48, 126.62, 128.02, 128.84, 131.71. ^{11}B NMR ($CDCl_3$): δ −17.88 (*q*, J_{B-H} = 94.2).

4.1.6. N,N,N-dibutylbenzylamine borane (*3c*)

White solid, m.p. = 67–68 °C, 35% (83 mg) yield. ^{1}H NMR ($CDCl_3$): δ 0.80–2.10 (v.*br* BH_3), 0.95 (*t*, 3H, J_{H-H} = 14.4), 1.28 (*m*, 2H), 1.79 (*m*, 2H), 2.61 (*t*, 2H, J_{H-H} = 16.8), 3.95 (*s*, 2H), 7.34 (*m*, 5H). ^{13}C NMR ($CDCl_3$) {H}: δ 13.80, 20.60, 25.59, 58.85, 63.27, 128.12, 128.74, 131.67, 132.26. ^{11}B NMR ($CDCl_3$): δ −13.69 (*q*, J_{B-H} = 90.10). *Anal.* Calc. for $C_{15}H_{28}NB$: C, 77.25; H, 12.02; N, 6.01. Found: C, 77.26; H, 12.04; N, 7.98%.

4.1.7. Dibenzylamine borane (*2d*)

It was obtained in a mixture with the starting material and the benzyl chloride although it was stirred after addition of the electrophile over-night at room temperature, it was stocked in the column and cannot be purified, the data could be reported from the crude mixture ^{1}H NMR ($CDCl_3$): δ 3.57 (*s*, 4H), 7.35 (*m*, 10H). ^{13}C NMR ($CDCl_3$): δ 58.67, 128.18, 128.9, 129.56, 130.22.

4.1.8. N,N,N-dimethylisopropylamine borane (*3e*)

Colorless oil, 25% (27 mg) yield. ^{1}H NMR ($CDCl_3$): δ 0.88 (*t*, 3H, J_{H-H} = 14.7), 1.10–2.18 (v.*br* BH_3), 1.26 (*d*, 6H, J_{H-H} = 7.8), 2.51 (*s*, 6H,), 3.06 (*m*, 1H). ^{13}C NMR ($CDCl_3$) {H}: δ 17.64, 48.41, 61.68. ^{11}B NMR ($CDCl_3$): δ −12.29 (*q*, J_{B-H} = 96.96).

4.1.9. N,N-propylisopropylamine borane (*2f*)

Colorless oil, 31% (35 mg) yield. ^{1}H NMR ($CDCl_3$): δ 0.89 (*t*, 3H, J_{H-H} = 14.7), 1.19 (*dd*, 6H, J^{1}_{H-H} = 6.6, J^{2}_{H-H} = 14.4), 1.60 (*m*, 2H), 1.80 (*m*, 1H), 2.62 (*m*, 1H), 3.19 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR

($CDCl_3$) {H}: δ 11.12, 17.87, 18.37, 20.36, 52.86, 54.07. ^{11}B NMR ($CDCl_3$): δ −18.32 (*q*, J_{B-H} = 95.04).

*4.1.10. N,N,N-dipropylisopropylamine borane (**3f**)*

Yellow oil, 15% (25 mg) yield. ^1H NMR ($CDCl_3$): δ 0.87 (*t*, 6H, J_{H-H} = 14.7), 1.23 (*d*, 6H, J_{H-H} = 6.6), 1.77 (*m*, 4H), 2.57 (*m*, 4H), 3.16 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 11.76, 16.27, 17.03, 58.28, 58.42. ^{11}B NMR ($CDCl_3$): δ −14.03 (*q*, J_{B-H} = 95.13).

*4.1.11. N,N-butylisopropylamine borane (**2g**)*

Yellow oil, 28% (40 mg) yield. ^1H NMR ($CDCl_3$): δ 0.91 (*t*, 3H, J_{H-H} = 14.4), 1.20 (*dd*, 6H, J^1_{H-H} = 6.6, J^2_{H-H} = 14.7), 1.31 (*m*, 2H), 1.55 (*m*, 1H), 1.72 (*m*, 1H), 2.66 (*m*, 2H), 3.20 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 13.91, 18.18, 18.77, 20.35, 29.51, 51.34, 54.37. ^{11}B NMR ($CDCl_3$): δ −18.31 (*q*, J_{B-H} = 93.21).

*4.1.12. N,N,N-dibutylisopropylamine borane (**3g**)*

Colorless oil, 18% (35 mg) yield. ^1H NMR ($CDCl_3$): δ 0.93 (*t*, 6H, J_{H-H} = 14.7), 1.23 (*d*, 6H, J_{H-H} = 6.9), 1.26 (*m*, 4H), 1.65 (*m*, 4H), 2.69 (*m*, 4H), 3.16 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 13.80, 17.03, 20.74, 24.96, 56.46, 58.25. ^{11}B NMR ($CDCl_3$): δ −14.06 (*q*, J_{B-H} = 89.66).

*4.1.13. N,N,N-dimethylt-butylamine borane (**3h**)*

White solid, m.p. = 110 °C, 40% (46 mg) yield. ^1H NMR ($CDCl_3$): δ 1.34 (*s*, 9H), 2.54 (*s*, 6H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 24.88, 47.39, 62.31. ^{11}B NMR ($CDCl_3$): δ −13.24 (*q*, J_{B-H} = 98.68). *Anal*. Calc. for $C_6H_{18}NB$: C, 62.61; H, 15.65; N, 12.17. Found: C, 62.70; H, 15.55; N, 12.11%.

*4.1.14. N,N-propylt-butylamine borane (**2i**)*

White solid, m.p. = 50–52 °C, 25% (35 mg) yield. ^1H NMR ($CDCl_3$): δ 0.91 (*t*, 3H, J_{H-H} = 15), 1.27 (*s*, 9H), 1.57 (*m*, 1H), 1.93 (*m*, 1H), 2.52 (*m*, 1H), 2.76 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 11.23, 21.90, 26.39, 52.40, 57.96. ^{11}B NMR ($CDCl_3$): δ −20.44 (*q*, J_{B-H} = 95.04). *Anal*. Calc. for $C_7H_{20}NB$: C, 65.12; H, 15.50; N, 10.85. Found: C, 65.19; H, 15.41; N, 10.80%.

*4.1.15. N,N-butylt-butylamine borane (**2j**)*

White solid, m.p. = 42 °C, 30% (44 mg) yield. ^1H NMR ($CDCl_3$): δ 0.92 (*t*, 3H, J_{H-H} = 14.4), 1.27 (*s*, 9H), 1.51 (*m*, 2H), 1.88 (*m*, 2H), 2.53 (*m*, 1H), 2.82 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 13.65, 20.15, 26.42, 30.89, 50.59, 58.04. ^{11}B NMR ($CDCl_3$): δ −20.26 (*q*, J_{B-H} = 92.16). *Anal*. Calc. for $C_8H_{22}NB$: C, 67.13; H, 15.38; N, 9.79. Found: C, 67.08; H, 15.42; N, 9.82%.

*4.1.16. N,N,N-methyldiisopropylamine borane (**3k**)*

Colorless oil, 15% (20 mg) yield. ^1H NMR ($CDCl_3$): δ 1.22 (*d*, 6H, J_{H-H} = 6.6), 1.33 (*d*, 6H, J_{H-H} = 6.6), 2.30 (*s*, 3H), 3.29 (*m*, 1H), BH_3 cannot be detected. ^{13}C NMR ($CDCl_3$) {H}: δ 16.99, 18.20, 39.93, 57.84. ^{11}B NMR ($CDCl_3$): δ −17.29 (*q*, J_{B-H} = 95.13).

4.2. Crystal structure analyses

Colorless single crystals of compounds **3a**, **3b** and **3c**, suitable for X-ray diffraction analysis were obtained from a saturated THF solution at 25 °C. The crystal data and structure refinement parameters are summarized in Table 2. All diffraction measurements were carried out on a Nonius KappaCCD diffractometer at ca. 110 K, using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation and 1° φ-scans. The intensity data was integrated and scaled by DENZO-SMN and Scalepack programs. The structures were solved by direct methods (SIR-97) [15], and refined by full-matrix least-squares on F^2 (SHELXL-97) [19].

Acknowledgements

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Appendix A. Supplementary material

Crystallographic data for the crystal structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-252714 (**2a**), CCDC-252716 (**3a**) and CCDC-252715 (**4a**). Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail:deposit@ccdc.cam.ac.uk).

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